A simplified electrochemically mediated ATRP synthesis of PEO-*b*-PMMA copolymers

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ABSTRACT

Poly(ethylene oxide)-*block*-poly(methyl methacrylate) amphiphilic copolymers were prepared *via* electrochemically mediated atom transfer radical polymerization (*e*ATRP) utilizing only 50 ppm of Cu^{II} complex, rather than previously reported concentrations of catalyst of *ca.* 1,000-30,000 ppm. The copolymers were also prepared *via* a simplified electrochemically mediated ATRP (*se*ATRP) procedure utilizing an aluminum wire sacrificial anode as a counter electrode, which was directly immersed into the reaction flask, without the need for its separation. This *se*ATRP system works under both potentiostatic and galvanostatic conditions. In each case the polymerization results showed similar molecular weight evolution while maintaining a narrow molecular weight distribution throughout the reactions. The successful chain extension and formation of block copolymers confirmed the living nature of the poly(alkyl methacrylates) prepared by *e*ATRP and *se*ATRP.

KEYWORDS

amphiphilic copolymers, poly(methyl methacrylate), simplified electrochemically mediated ATRP

INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most versatile reversible deactivation radical polymerization (RDRP) methods, one that allows control over macromolecular topology[1-11] and synthesis of polymers with unique structures from a multiplicity of monomers, including (meth)acrylates, (meth)acrylamides, styrenes, acrylonitrile and vinyl pyridine.[12-20]

Amphiphilic segmented copolymers composed of a poly(methyl methacrylate) (PMMA) covalently linked to a poly(ethylene oxide) (PEO) are especially interesting, because they can be used in biomedical applications, including drug delivery and tissue engineering, due to their unique properties such as solubility, crystallinity, and flexibility.[21-30] The use of PEO in this class of segmented polymers is related to its biocompatibility, hydrophilicity and solubility in both water and common organic solvents.[23, 31, 32] Furthermore PMMA is of interest because of its resistance to enzymatic attack, biocompatibility, and high optical qualities.[33, 34] Previously a number of block copolymers were synthesized using a PEO macroinitiator, for example PEO-*b*-PMMA with narrow molecular weight distribution (MWD) ($M_w/M_n = 1.05-1.33$) was prepared by ATRP. However rather high catalyst loadings, *ca.* 1,000–30,000 ppm, were used.[23, 24, 35-37] Triblock copolymers with narrow MWD ($M_w/M_n = 1.11-1.30$) were prepared using a difunctional PEO macroinitiator but also required a high concentration of catalyst, at least 10,500 ppm.[23, 38, 39]

Recently, new ATRP procedures with low concentration of Cu-based catalysts were developed. They include activators regenerated by electron transfer (ARGET),[40-45] initiators for continuous activator regeneration (ICAR),[40, 46, 47] or supplemental activators and reducing agents (SARA)[48-52] ATRP methods. More recently, physical means of regeneration of low ppm activators were developed, including light[53-65] and electrical current.[20, 66-74] Electrochemically mediated ATRP (*e*ATRP) has attracted a great deal of

attention because of its low catalyst loading, improved tolerance toward oxygen, elimination of chemical reducing agents and capability of catalyst removal through electrodeposition. Based on the mechanism of *e*ATRP, the ratio of the concentration of $\text{Cu}^{\text{I}}/\text{L}$ to $\text{X-Cu}^{\text{II}}/\text{L}$ can be precisely controlled by the applied current (I), and potential (E) at the electrode surface[68] and consequently, the concentration of the radical species required to propagate and form polymeric chains by reacting with monomers (M), and the efficiency of deactivation back to the dormant species ($\text{P}_n\text{-X}$) can be controlled, **Scheme 1**. This allows for controlled synthesis of polymers with complex architectures.[69, 70, 75, 76]

Scheme 1. Mechanism of *e*ATRP. Reprinted with permission from.[68] Copyright 2013 American Chemical Society.

However, there are some limitations associated with *e*ATRP, especially in the reaction setup stage. Typically, *e*ATRP polymerizations can be achieved by utilizing a three electrode system under potentiostatic conditions. Recently,[73] a significant simplification of the procedures used for an *e*ATRP was reported. A use of sacrificial counter electrode allows to eliminate the separation of electrode compartments and to perform polymerization process both under potentiostatic and galvanostatic conditions.

This paper details the preparation of diblock poly(ethylene oxide)-*block*- poly(methyl methacrylate) copolymers, (PEO-*b*-PMMA) (**Scheme 2**) and triblock poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-poly(*t*-butyl acrylate) (PEO-*b*-PMMA-*b*-PtBA) copolymers (**Scheme 3**) by *e*ATRP and simplified electrochemically mediated ATRP

(*se*ATRP) under both potentiostatic and galvanostatic conditions. Polymerization conditions were optimized to provide fast reactions while employing low catalyst concentrations and maintaining narrow molecular weight distributions.

Scheme 2. Synthesis of PEO-*b*-PMMA copolymers via *e*ATRP or *se*ATRP.

Scheme 3. Synthesis of PEO-*b*-PMMA-*b*-PtBA copolymers via *se*ATRP.

RESULTS AND DISCUSSION

Well-controlled ATRP synthesis of block copolymers is challenging when chain extension occurs from a macroinitiator of lower activity to a more active monomer. The rate of activation of a bromo-terminated polymethacrylate chain end is faster than the activation of a 2-bromoisobutyrate PEO chain end.[39, 77-82] Typically, halogen exchange procedures[23, 24, 35-39] are employed to solve this problem, but they can not be used for systems with low concentrations of catalyst, because of poor initiation efficiency. Motivated by the very good control over the polymerization that is attainable with high amounts Cu (*ca.* 1,000-30,000 ppm)[23, 24, 29, 35-39] we initially set out to achieve similar levels of control using only 50

ppm of Cu^{II} /L in solution, following the *e*ATRP procedure under potentiostatic conditions, which requires a three electrode system – a Pt mesh working electrode (WE), a Pt mesh counter electrode (CE) (separated from the reaction media using methylated cellulose gel), and a saturated calomel electrode (SCE) reference electrode (RE). In addition, to simplify the procedure, *e*ATRP was carried out under galvanostatic conditions, which only requires a Pt mesh working cathode and an Al wire counter/sacrificial anode.

Table 1 summarizes results of the block copolymers synthesis using poly(ethylene oxide) macroinitiators (PEO MI, $M_n = 2000$, $M_w/M_n = 1.04$).

Table 1. Summary of PEO-*b*-PMMA and PEO-*b*-PMMA-*b*-PBA synthesis by *e*ATRP and *se*ATRP.

entry	[M]/[MI]/ [$\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}$]	[MI] (mM)	$E_{\text{app}}^{\text{a}}$ (vs. SCE)	k_p^{app} (h^{-1}) ^b	conv (%) ^b	$M_{n,\text{theo}}$ ($\times 10^{-3}$) ^c	M_n^{app} ($\times 10^{-3}$) ^b	M_w/M_n^{d}
1	300/1 ^e /0.06	15.6	$E_{\text{pc}}-40$ mV	0.867	93	30.0	28.5	1.41
2	300/1 ^e /0.03	15.6	$E_{\text{pc}}-40$ mV	0.808	90	29.1	30.4	1.13
3	300/1 ^e /0.015	15.6	$E_{\text{pc}}-40$ mV	0.449	75	24.5	24.9	1.21
4	400/1 ^e /0.04	11.7	$E_{\text{pc}}-40$ mV	0.766	89	37.6	35.4	1.26
5	500/1 ^e /0.05	9.3	$E_{\text{pc}}-40$ mV	0.504	79	41.0	44.3	1.23
6	500/1 ^e /0.05	9.3	Galvanostatic Conditions ^f	0.457	75	39.7	38.9	1.24
7	500/1 ^e /0.05	9.3	$E_{\text{pc}}-40$ mV	0.601	84	43.8	41.8	1.12
8	500/1 ^e /0.05	9.3	Galvanostatic Conditions ^g	0.460	76	40.1	42.1	1.13
9	300/1 ^h /0.015	7.2	$E_{\text{pc}}-80$ mV	0.165	65	55.4	53.0	1.13

Conventional *e*ATRP under potentiostatic conditions (WE = Pt mesh, CE = Pt mesh separated from the reaction solution by the supporting electrolyte saturated Tylose gel, RE = SCE): entries 1–5; *e*ATRP under galvanostatic conditions (WE and CE without RE): entry 6; *se*ATRP under potentiostatic conditions (WE = Pt mesh, CE = Al

wire ($l = 10$ cm, $d = 1$ mm), RE = SCE): entry 7 and 9; *se*ATRP under galvanostatic conditions: entry 8. ^a E_{app} were selected based on CV analysis ($v = 100$ mV/s); ^bMonomer conversion, apparent M_n and k_p were determined by NMR; ^c $M_{n,theo} = ([M]_0/[MI]_0) \times \text{conversion} \times M_{monomer} + M_{PEOMI}$; ^dMWD was determined by THF GPC with PS standard curves; ^f $I_{app} = -1.00, -0.70, -0.37, -0.14,$ and -0.06 mA for each steps; ^g $I_{app} = -0.60, -0.42, -0.35, -0.29, -0.23,$ and -0.16 mA for each steps. General reaction conditions: $T = 50$ °C; $V_{tot} = 20$ mL (in DMF); $[M]$ (MMA) = 4.7 M (except entry 9 (*t*BA) = 2.2 M); $[Cu^{II}Br_2/2TPMA] = 0.47$ mM (except entry 1 = 0.93 mM, entry 3 = 0.23 mM and entry 9 = 0.22 mM); Supporting electrolyte concentration (tetrabutylammonium perchlorate, TBAP) = 0.2 M; ^eMI = poly(ethylene oxide) macroinitiators (PEO MI); ^hMI = poly(ethylene oxide)-*b*-poly(methyl methacrylate) macroinitiator (PEO-*b*-PMMA-Br).

Influence of $[Cu^{II}/Br_2/2TPMA]_0$. Three polymerizations were conducted using different $[X-Cu^{II}/L]_0$ ranging from 200 to 50 ppm (**Table 1, entries 1–3, Figure 1a,b, S1, 2a,b, and S3a–c**). According to the equation describing the distribution of molecular weights of polymer: $\frac{M_w}{M_n} = 1 + \left(\frac{k_p[P-X]}{k_{da}[Cu^{II}]} \right) \left(\frac{2}{p} - 1 \right)$, [68] where p denote monomer conversion, higher concentrations of copper should yield faster rates of polymerization (defined as $R_p = k_p[M][P \cdot] = k_p[M]K_{ATRP} \frac{[P-X][Cu^I/L]}{[X-Cu^{II}/L]}$) and lower M_w/M_n values). [68] Therefore, apparent propagation constants (k_p^{app}) were measured to investigate the effect of the concentration of the catalyst complex. As the $[X-Cu^{II}/L]_0$ increases, the rate of polymerization increases with a near square root dependence (**Figure 1a**), similar to other literature accounts which indicate faster rates with higher catalyst loadings.[44] An increase in R_p reflects a higher $[P \cdot]$, which is a result of faster reduction rates, generating more Cu^I/L . Moreover, as **Figure 1a** illustrates, while there is a linear increase in molecular weight (MW) with respect to conversion for all reactions, there is a decrease in the MWDs for lower $[X-Cu^{II}/L]_0$ (compare M_w/M_n ; of **entries 2 vs. 3 Table 1**;; with **entry 1** which represents 200 ppm catalyst concentration and results in broader MWD value from higher R_p).

Fig. 1. eATRP of methyl methacrylate as a function of $[X-Cu^{II}/L]$. (a) First-order kinetic plot of monomer conversion versus time, and (b) M_n and M_w/M_n versus monomer conversion. Reaction conditions: $[MMA]/[PEO MI]/[Cu^{II}Br_2/2TPMA] = 300/1/x$, $[MMA] = 4.7$ M in DMF, $[Cu^{II}Br_2/2TPMA] = 0.47$ mM, $T = 50$ °C, $[TBAP]_0 = 0.2$ M, $V_{tot} = 20$ mL, $E_{app} = E_{pc} - 40$ mV (vs. SCE), $x = 0.06, 0.03$, and 0.015 corresponding to 200, 100, and 50 ppm, respectively.

Current profiles (**Figure S1**) indicate that an increased concentration of electroactive species results the highest current values. $E_{1/2}$ values for Br-Cu^{II}/TPMA complex conducted in the absence and presence of a PEO MI are reported in the Supporting Information (**Figure S2a**). The CV response of X-Cu^{II}/L drastically changed when the initiator was added; the cathodic peak approximately doubled in height while the anodic one decreased, clearly indicating that Cu^I/L rapidly reacted with PEO MI. The results indicate that higher concentrations of catalysts result in faster reaction with alkyl halide and thus faster creation of radical species and Cu^{II}/L. Briefly, a polymerization with 200 ppm catalyst concentration was 2 times faster (compare k_p^{app} ; **Table 1, entries 1 vs. 3**) than with 50 ppm.[20, 68] Furthermore, the lowest concentration of catalyst complex (50 ppm) generates transparent solutions and represents a 10–600 fold decrease in X-Cu^{II}/L concentration relative to previous reports of *ca.* 1,000–30,000 ppm Cu^I/L used in ATRP[24, 29, 35-37, 39] and 500 ppm Cu^I/L used in ARGET ATRP.[83]

Under the optimal concentration of the catalyst complex (100 ppm), all of PMMA blocks had narrow MWD. The MWD of the second block can be determined by equation: $Y_{\text{PEO-PMMA}} = w_{\text{PEO}}^2 Y_{\text{PEO}} + w_{\text{PMMA}}^2 Y_{\text{PMMA}}$, where w is weight fraction of each block and $Y = \bar{D} - 1$ [84] ($\bar{D}$ denote dispersity). The weight fraction of PMMA was 0.82 (**Table 1, entry 2**) based on monomer consumption, therefore the calculated MWD of PMMA block was 1.19, indicating well-defined polymers synthesized by *e*ATRP.

Effect of targeted degree of polymerization. The next series of polymerizations were investigated in the presence of X-Cu^{II}/L complex and were designed to probe the influence of initial molar ratio of MMA (M) to PEO MI (MI) on the diblock copolymer formation, **Table 1, entries 2,4–5**, (**Figure 2a,b**, **S3b,d,e** and **S4**). Well controlled copolymers were attained using *e*ATRP with 100 ppm of X-Cu^{II}/L. These polymerizations were performed at three different ratios of $[M]_0/[MI]_0 = 300, 400$, and 500 , targeting different DPs. To investigate the effect of targeted DP, k_p^{app} was measured and compared to the initiator concentration. The values of k_p^{app} increased linearly with $[MI]_0$ (**Figure 2a**). Moreover, MW evolution was well-matched with the theoretical values (**Figure 2b**) and maintained narrow MWD (**Figure S3b,d,e**). A slightly higher k_p^{app} and monomer conversion >90% was obtained for the polymerizations carried out with the highest concentration of PEO MI ($[M]_0/[MI]_0 = 300$; compare k_p^{app} ; **Table 1, entries 2 vs. 4–5**) which can be attributed to the fact that the presence of higher concentrations of MI could suppress the fraction of terminated chains and reduce MWD.[70]

Fig. 2. *e*ATRP of methyl methacrylate as a function of targeted DP (300, 400, and 500). (a) First-order kinetic plot of monomer conversion versus time, and (b) M_n and M_w/M_n versus monomer conversion. Reaction conditions: [MMA] = 4.7 M in DMF, [Cu^{II}Br₂/2TPMA] = 0.47 mM, T = 50 °C, [TBAP]₀ = 0.2 M, V_{tot} = 20 mL, $E_{\text{app}} = E_{\text{pc}} - 40$ mV (vs. SCE).

Simplification of the reaction setup. The polymerization under galvanostatic conditions was carried out and the results are reported in **Table 1, entry 6, Figure 3a,b, S3f, and 5**. The applied currents (I_{app}) were determined by the polymerizations conducted under potentiostatic conditions, **Table 1, entry 5, Figure 3a,b, S3e, and 5**. On the basis of the chronoamperometry (CA) results (**Figure 3a**), the total charge passed was calculated by integration of the CA area ($I = Q/s$), hence, five constant I_{app} were used for the galvanostatic polymerization, where negative values indicate cathodic current. The R_p showed a slight decrease from values observed under potentiostatic conditions, compare k_p^{app} ; **Table 1, entries 6 vs. 5**. Moreover, identical first-order kinetic plots were observed (**Figure S5**), and GPC analysis indicated similar MW evolution and narrow MWD, **Figure 3b**.

Fig. 3. Multi-step chronoamperometry for galvanostatic *e*ATRP; (a) chronoamperometry results from potentiostatic conditions (exponential drop) and applied current (red line), and (b) M_n and M_w/M_n versus monomer conversion by potentiostatic and galvanostatic conditions.

The results of polymerization under potentiostatic conditions with a Pt mesh WE, a sacrificial Al CE, and SCE RE are shown in **Table 1, entry 7**, and in **Figure 4a,b, S3g**, and **6**. A first-order kinetic plot was once again observed, **Figure S6**, and GPC analysis indicated linear MW evolution and even narrower MWD, **Figure 4b**. Subsequently a constant I_{app} were used for the galvanostatic polymerization, **Table 1, entry 8**, **Figure 4a,b, S3h**, and **6**. The values observed for *se*ATRP under galvanostatic conditions showed similar MW evolution and MWD values compared to polymerizations conducted under potentiostatic conditions, **Figure 4b**.

Fig. 4. Multi-step chronoamperometry for galvanostatic *se*ATRP; (a) chronoamperometry results from potentiostatic conditions (exponential drop) and applied current (red line), and (b) M_n and M_w/M_n versus monomer conversion by potentiostatic and galvanostatic conditions.

Chain extension experiments. Chain end functionality was evaluated by chain extension from a macroinitiator to form a triblock copolymer. A PEO-*b*-PMMA-Br with high DP was prepared by *e*ATRP with $M_n=30,400$ and $M_w/M_n=1.13$ (**Table 1, entry 2, Figure 1a,b, S1, 2a,b, S3b, and 8**) then used in a chain extension polymerization with *tert*-butyl acrylate (*t*BA) as the second monomer in a *se*ATRP (**Figure S9**). Linear first-order kinetics was observed (**Figure S7**) and GPC traces indicated successful chain extension with *t*BA, as shown a clean shift in the MW peak toward higher MW, **Figure 5b**. The MW evolution with conversion followed the theoretical MW indicating high initiation efficiency, **Figure 5a**. This result confirms that the halogen end groups are preserved during the *e*ATRP of MMA.

Fig. 5. Chain extension by *se*ATRP; (a) M_n and M_w/M_n versus monomer conversion, and (b) GPC results of the formed block copolymer. Reaction conditions: $[tBA]/[PEO\text{-}b\text{-}PMMA\text{-}Br]/[Cu^{II}Br_2/2TPMA] = 300/1/0.015$, $[tBA] = 2.2$ M in DMF, $[Cu^{II}Br_2/2TPMA] = 0.22$ mM, $T = 50$ °C, $[TBAP]_0 = 0.2$ M, $V_{tot} = 20$ mL, $E_{app} = E_{pc} - 80$ mV (vs. SCE).

CONCLUSIONS

Electrochemically mediated atom transfer radical polymerization (*e*ATRP) of methyl methacrylate was investigated under a variety of conditions, including catalyst concentration, and monomer to macroinitiator molar ratio, targeted DP. The synthesis of poly(ethylene oxide)-*block*-poly(methyl methacrylate) copolymers was carried out, utilizing low concentrations of catalyst, 50 ppm of Cu^{II} species. The copolymers were also prepared *via* a simplified electrochemically mediated ATRP (*se*ATRP) procedure under both potentiostatic and galvanostatic conditions. The use of a multi-step current galvanostatic procedure provided identical results to polymerizations carried out under potentiostatic conditions, with both cases giving polymers with molecular weight evolution close to theoretical values and generating polymers with narrow molecular weight distribution. Chain extension of the formed block copolymer with *t*BA confirmed the preservation of terminal halogen end group during the *e*ATRP of methacrylates.

Conflict of interest

The authors declare no competing financial interest.

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Associated Content

Supporting Information – Experimental conditions, figures showing GPC traces of polymers, NMR spectrum, CV and CA results.

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A simplified electrochemically mediated ATRP synthesis of PEO-*b*-PMMA copolymers

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Electrochemically mediated atom transfer radical polymerization (*e*ATRP) and simplified electrochemically mediated ATRP (*se*ATRP) of methyl methacrylate were well controlled with low concentration of Cu^{II}Br₂/TPMA complex under potentiostatic or galvanostatic conditions. Diblock copolymers with molecular weights close to theoretical values and with narrow molecular weight distribution were prepared.

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